

Hydrogen-Bonded Supramolecular Assembly of Porphyrins

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Beamline(s): X7B

Introduction: Self-assembly into specifically designed structures involves the spontaneous association of molecules through intermolecular interactions. Designed porphyrin arrays have been formed by hydrogen bonding, axial metallo-porphyrin coordination, and coordination of exocyclic ligands. While there is an ever-increasing number of discrete porphyrin arrays mediated by metal ion coordination, there are few mediated by hydrogen bonding. As a result, two new sets of porphyrin building blocks bearing rigidly linked peripheral hydrogen bonding moieties have been synthesized [1]. With these complementary synthons, it is possible to form various types of rigid multi-porphyrin arrays with different designed spatial relationships. An X-ray study of one of these new derivatives **1** reveals an unexpected new mode of hydrogen-bonded supramolecular aggregation mediated by adventitious water molecules [2].

Methods and Materials: Single crystals of **1** were grown from a mixture of ethyl acetate and hexane, but the crystals do not incorporate either of these solvents. Instead, the lattice contains 2.5 molecules of adventitious water per porphyrin that mediate an extensive supramolecular array via multiple hydrogen bonds. Two hemispheres of data were collected at 100K by the rotation method using a MAR345 image plate detector. The data were processed and merged with Denzo/Scalepack [3] and the structure was solved and refined with the SHELXTL package [4].

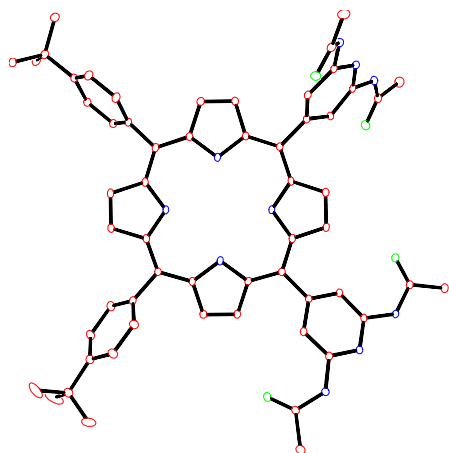
Results: The molecular structure of **1** is shown in Figure 1 and its novel self-assembly is shown in Figure 2.

Conclusions: These results demonstrate that water can mediate the self-aggregation of H-bonding species and dictate the supramolecular arrangement of subunits, as it does in many protein structures.

Acknowledgments: We thank Dr. Jonathan C. Hanson for assistance with the crystallographic data collection. The work at Brookhaven was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC02-98CH10886.

References:

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- 2 X. Shi, K.M. Barkigia, J. Fajer, and C.M. Drain, *J. Org. Chem.*, in press.
- 3 Z. Otwinowski and W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode," *Methods in Enzymology*, Volume **276**: Macromolecular Crystallography, part A, p. 307-326, 1997, C. W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.
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Figure 1. Molecular structure of a new porphyrin building block. Carbons are shown as red, nitrogens as blue, and oxygens as green. Hydrogens are omitted for clarity. The crystal used in this work measured 0.175x0.15x0.006 mm.

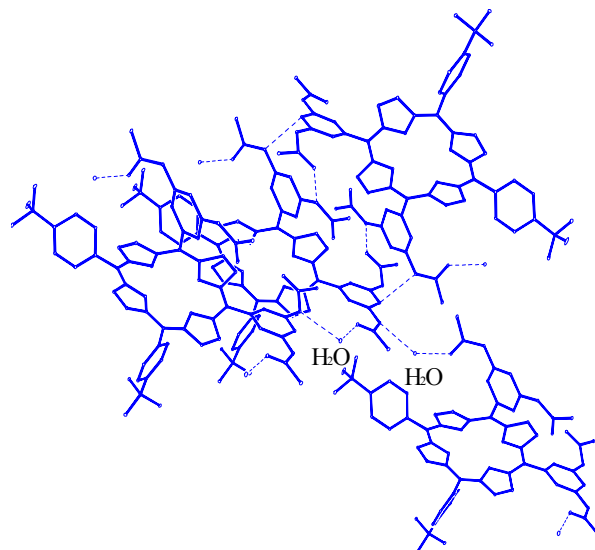


Figure 2. Hydrogen-bonded supramolecular assembly of **1**, mediated by water molecules. Hydrogen bonds are shown as dotted lines. Only 2 of the 2.5 unique water molecules are shown and labeled.